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Vapor–Liquid Equilibria for the Systems Butyl Acetate + Polystyrene and Diethyl Ether + Poly(butyl methacrylate)

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Vapor–liquid equilibria (VLE) for butyl acetate + polystyrene with five different molar masses at 308.15 K and for diethyl ether + poly(butyl methacrylate) with three different molar masses at 298.15 K measured by the static quartz-spring gravimetric method are presented. For the first system, the reduced pressure p_1/p_1° versus mass fraction w_1 of solvent 1 was found to be independent of the molar mass of the polymer within experimental error, while for the second system, a notable dependence was observed. Flory–Huggins parameters χ calculated from the VLE results are also presented which show not only a concentration dependence, but also a weak molar-mass dependence for the first system and a strong molar-mass dependence for the second system.

Introduction

Vapor–liquid equilibria (VLE) for polymer solutions have been extensively studied since the 1960s. The interest stemmed not only from the highly nonideal behavior of those solutions but also from industrial requirement. VLE results are required for the design and development of processes and equipment in both polymer manufacturing and polymer processing. Bonner (*1*) presented a comprehensive review regarding experimental methods, theories, and published data on this subject.

Polymers are characterized by their high and changeable molar masses. Besides, industrial polymers are always polydisperse. The effect on polymer properties due to different molar masses has attracted attention in the polymer field over the years. For liquid–liquid equilibria (LLE), a remarkable effect has been observed (*2*). Generally, the larger the molar mass of th epolymer, the higher the upper-critical-solution temperature (UCST) and the more depressed the lower-critical-solution temperature (LCST). In extreme cases, an hourglass-shaped phase diagram will appear. However, for vapor–liquid equilibria, usually the molar-mass dependence is small (*3, 4*). In this work, we present VLE results for the system butyl acetate + polystyrene with five different molar masses covering the wide range from 2980 to 3840 × 10^3 which shows that the molar mass of polystyrene does not affect the VLE for this system within experimental error. The VLE results for the system diethyl ether + poly(butyl methacrylate) with three different molar masses from 17 300 to 88 100 show a definite molar-mass dependence.

For theoretical interest, the Flory–Huggins parameter χ (*5*) is often used to characterize the solvent–polymer interaction for polymer solutions and polymer–polymer interaction for polymer blends. Reliable results for the parameter χ are important not only for explaining polymer properties such as the solvent effect and the compatibility between different polymers but also for developing theories to correlate the molecular structure with the properties. In this work, the Flory–Huggins parameters and their dependence on the concentration and on the molar mass calculated from the VLE results are presented.

Experimental Section

There are three methods frequently employed to measure VLE in polymer solutions: the static quartz-spring gravitational method (*6, 7*), the chromatographic method (*8*), and the piezoelectric method (*9*). Generally, the first one is often used as a standard method because of its rigorous principle and high precision. Although the time needed for determination is quite long, sometimes, especially when the polymer sample is in the crystalline state and when the solubility of the solvent is low, an equilibrium time of several days is usual. However, the method is still the first choice because of its reliability. For the second method, although it is more efficient, it is more suitable for determining infinite-dilution activity coefficients. The third method is still under development.

In this work, we use the static quartz-spring gravimetric method. A multiple-cell apparatus similar to that used by Panayiotou and Vera (*7*) was constructed which has six cells as shown in Figure 1. Each cell is equipped with a quartz spring with two sample baskets hung under to enhance the surface contact between the sample and the vapor. All the cells are immersed in an air-thermostat bath, the temperature of which is maintained within ±0.01 K. To avoid contamination of vacuum grease by the solvent, all movable parts are connected by stainless steel unions. The vacuum system was checked to ensure that a pressure of less than 1 Pa could be maintained in the system for over a week. The relative error of the measured pressure is estimated to be ±0.1%, restricted by the precision of the cathetometer which is used to record the height of the mercury column. The relative error of the amount of vapor absorbed per unit mass of the sample is determined from the sensitivity of the quartz spring and is about 0.5% which is the largest error in the experiment. Because of the long time for equilibrium, some unexpected deficiencies may happen during the experiment. Therefore, the total relative error for the reduced pressure p_1/p_1°

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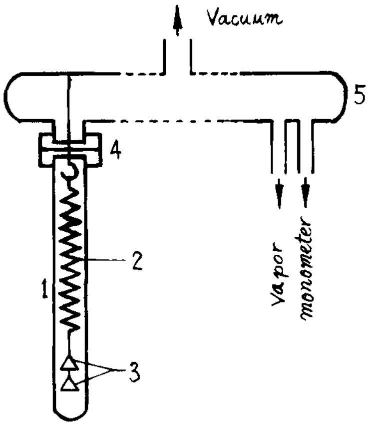

Figure 1. Schematic diagram for the apparatus: 1, absorption cell; 2, quartz spring; 3, aluminum sample basket; 4, stainless steel union; 5, horizontal chamber.

Table 1. Molecular Parameters of Polystyrene and Poly(butyl methacrylate)

polystyrene		poly(butyl methacrylate)	
M_w	M_w/M_n	M_w	M_w/M_n
3.84×10^6	1.04	88.1×10^3	1.09
1.90×10^5	1.04	37.9×10^3	1.07
3.79×10^4	1.01	17.3×10^3	1.06
9.10×10^3	1.02		
2.98×10^3	1.11		

versus mass fraction w_1 for the solvent (1) is estimated to be as high as 1%, where $p_1°$ is the vapor pressure of the pure solvent. The reliability of the apparatus has been checked by comparing VLE measurements on the system toluene + polystyrene with literature data (*4*).

Solvents. Analytical-reagent-grade butyl acetate and diethyl ether were first dried over calcium chloride and then rectified with a distillation column and collected at constant normal boiling temperatures of 399.2 and 307.6 K (*10*), respectively. After being charged into a solvent cell attached to the apparatus, the solvents were further carefully degassed prior to the experiment by a combination of total reflux distillation under vacuum and freezing–thawing processes.

Polystyrene. Samples of different molar masses were purchased from Tosoh Co. in Japan. Relative weight-average molar masses M_w and corresponding polydispersity indices M_w/M_n for those samples are listed in Table 1, where M_n is the relative number-average molar mass.

Poly(butyl methacrylate). Samples of different molar masses were synthesized in the Polymer Research Laboratory of East China University of Science and Technology in Shanghai, China. Relative weight-average molar masses M_w and corresponding polydispersity indices M_w/M_n for those samples are also listed in Table 1.

VLE Results

The VLE results of $p_1/p_1°$ and w_1 for the system butyl acetate (1) + polystyrene (2) at 308.15 K and for the system diethyl ether + poly(butyl methacrylate) at 298.15 K are listed in Tables 2 and 3, respectively. Figures 2 and 3 show the corresponding plots. As shown in Figure 2, almost all the data points for five polystyrene samples with different molar masses fall on a single curve within experimental error. In view of the wide range of molar masses from 2980 to 3840 × 10^3 for the polystyrene samples, the molar mass of polystyrene is obviously not an important factor in the VLE results. However, as shown in Figure 3, results for three poly(butyl methacrylate) samples with different molar masses from 17 300 to 88 100 are distinguished by three different curves. The dependence of the VLE results on the molar mass of poly(butyl methacrylate) is remarkable.

Table 2. Experimental Results for Butyl Acetate (1) + Polystyrene (2) at 308.15 K

$p_1/p_1°$	w_1	ϕ_1	γ_w	$p_1/p_1°$	w_1	ϕ_1	γ_w
$M_{w,2} = 3.84 \times 10^6$				$M_{w,2} = 1.90 \times 10^5$			
0.1573	0.0321	0.0392	4.915	0.1573	0.0321	0.0392	4.915
0.2980	0.0620	0.0751	4.818	0.2980	0.0620	0.0751	4.818
0.4674	0.1134	0.1358	4.129	0.4674	0.1092	0.1309	4.288
0.6502	0.1711	0.2023	3.805	0.5262	0.1445	0.1719	3.648
0.6996	0.1977	0.2324	3.542	0.6996	0.1946	0.2290	3.599
0.7510	0.2183	0.2555	3.443	0.7510	0.2509	0.2916	2.996
0.8332	0.2763	0.3194	3.017	0.8332	0.2944	0.3390	2.832
0.8621	0.2963	0.3410	2.911	0.8621	0.3172	0.3634	2.719
0.9365	0.3640	0.4129	2.573	0.9229	0.3644	0.4133	2.533
$M_{w,2} = 3.79 \times 10^4$				$M_{w,2} = 9.10 \times 10^3$			
0.2980	0.0409	0.0498	7.304	0.3657	0.0835	0.1007	4.389
0.4883	0.1068	0.1281	4.580	0.5232	0.1286	0.1535	4.075
0.5262	0.1210	0.1447	4.356	0.5731	0.1491	0.1772	3.849
0.5835	0.1432	0.1704	4.081	0.6766	0.1770	0.2091	3.827
0.6766	0.1730	0.2045	3.915	0.8331	0.2440	0.2840	3.416
0.6996	0.1383	0.2168	3.810	0.8610	0.2750	0.3179	3.132
0.8332	0.2615	0.3032	3.188	0.8789	0.3083	0.3539	2.852
0.8790	0.3622	0.4110	2.428	0.9587	0.3852	0.4350	2.489
0.9229	0.3711	0.4203	2.488	0.9727	0.4394	0.4906	2.214
$M_{w,2} = 2.98 \times 10^3$							
0.3657	0.0804	0.0970	4.558				
0.5232	0.1200	0.1435	4.367				
0.6637	0.1702	0.2013	3.904				
0.7893	0.2202	0.2576	3.587				
0.8331	0.2555	0.2966	3.263				
0.8520	0.2678	0.3101	3.183				
0.8610	0.2912	0.3355	2.958				
0.8840	0.3176	0.3639	2.785				
0.9209	0.3333	0.3806	2.764				

Table 3. Experimental Results for Diethyl Ether (1) + Poly(butyl methacrylate) (2) at 298.15 K

$p_1/p_1°$	w_1	ϕ_1	γ_w	$p_1/p_1°$	w_1	ϕ_1	γ_w
$M_{w,2} = 88.1 \times 10^3$				$M_{w,2} = 37.9 \times 10^3$			
0.1966	0.0257	0.0390	7.462	0.1866	0.0415	0.0624	4.621
0.3019	0.0350	0.0528	8.831	0.3019	0.0611	0.0910	5.059
0.4103	0.0673	0.0999	6.219	0.4103	0.0825	0.1215	5.073
0.5089	0.0852	0.1253	6.073	0.5089	0.1079	0.1569	4.795
0.6044	0.1143	0.1656	5.359	0.6044	0.1331	0.1910	4.602
0.7226	0.1647	0.2327	4.429	0.7226	0.1774	0.2491	4.111
0.7975	0.2096	0.2897	3.831	0.7975	0.2165	0.2983	3.709
0.8954	0.2819	0.3765	3.187	0.8954	0.2819	0.3902	3.058
0.9329	0.3469	0.4496	2.695	0.9329	0.3469	0.4643	2.594
$M_{w,2} = 17.3 \times 10^3$							
0.1866	0.0522	0.0781	2.549				
0.3019	0.0689	0.1022	4.486				
0.4103	0.0945	0.1383	4.429				
0.5089	0.1138	0.1649	4.546				
0.6044	0.1448	0.2066	4.230				
0.7226	0.2027	0.2811	3.598				
0.7975	0.2437	0.3314	3.295				
0.8954	0.3326	0.4339	2.244				
0.9329	0.4188	0.5257	2.233				

In Tables 2 and 3, volume fractions of the solvent ϕ_1 and the mass-based activity coefficient of the solvent γ_w are also listed. The former is defined by

$$\phi_1 = \frac{m_1 v_1}{m_1 v_1 + m_2 v_2} \qquad (1)$$

where m_1, v_1, m_2, and v_2 are masses and specific volumes for the solvent (1) and polymer (2), respectively. The latter is calculated by

Table 4. Smoothed Results for Butyl Acetate (1) + Polystyrene (2) at 308.15 K

				χ				
p_1/p_1°	w_1	ϕ_1	γ_w	$10^{-3}M_{w,2} = 3840$	$10^3M_{w,2} = 1900$	$10^3M_{w,2} = 379$	$10^3M_{w,2} = 9.10$	$10^3M_{w,2} = 2.98$
0.1000	0.0178	0.0218	5.624	0.5712	0.5721	0.5751	0.5872	0.6204
0.2000	0.0377	0.0459	5.324	0.5718	0.5727	0.5757	0.5881	0.6221
0.3000	0.0598	0.0725	5.033	0.5763	0.5773	0.5804	0.5932	0.6281
0.4000	0.0850	0.1025	4.719	0.5799	0.5809	0.5841	0.5973	0.6334
0.5000	0.1146	0.1372	4.374	0.5811	0.5821	0.5854	0.5992	0.6368
0.6000	0.1495	0.1776	4.022	0.5869	0.5879	0.5914	0.6058	0.6452
0.7000	0.1930	0.2271	3.633	0.5933	0.5944	0.5981	0.6135	0.6554
0.8000	0.2505	0.2912	3.198	0.6037	0.6048	0.6090	0.6258	0.6714
0.9000	0.3370	0.3845	2.674	0.6231	0.6234	0.6291	0.6485	0.7009

Table 5. Smoothed Results for Diethyl Ether (1) + Poly(butyl methacrylate) (2) at 298.15 K

p_1/p_1°	w	ϕ_1	γ_w	χ	p_1/p_1°	w_1	ϕ_1	γ_w	χ
	$M_{w,2} = 88.1 \times 10^3$					$M_{w,2} = 37.9 \times 10^3$			
0.1000	0.0129	0.0197	7.990	0.7030	0.1000	0.0148	0.0226	6.965	0.5692
0.2000	0.0277	0.0420	7.417	0.6878	0.2000	0.0315	0.0476	6.523	0.5645
0.3000	0.0448	0.0673	6.856	0.6746	0.3000	0.0508	0.0764	6.046	0.5561
0.4000	0.0650	0.0966	6.279	0.6603	0.4000	0.0732	0.1083	5.576	0.5503
0.5000	0.0890	0.1306	5.713	0.6494	0.5000	0.1006	0.1468	5.055	0.5382
0.6000	0.1205	0.1741	5.047	0.6247	0.6000	0.1347	0.1932	4.515	0.5260
0.7000	0.1621	0.2293	4.362	0.6000	0.7000	0.1793	0.2515	3.944	0.5131
0.8000	0.2247	0.3083	3.584	0.5631	0.8000	0.2441	0.3319	3.300	0.4939
0.9000	0.3246	0.4250	2.782	0.5426	0.9000	0.3544	0.4579	2.548	0.4720
0.9300	0.3780	0.4831	2.466	0.5280	0.9300	0.4116	0.5183	2.265	0.4600
	$M_{w,2} = 17.3 \times 10^3$								
0.1000	0.0162	0.0247	6.363	0.4833					
0.2000	0.0346	0.0522	5.938	0.4763					
0.3000	0.0560	0.0836	5.485	0.4654					
0.4000	0.0811	0.1195	5.033	0.4560					
0.5000	0.1117	0.1621	4.552	0.4430					
0.6000	0.1502	0.2137	4.049	0.4279					
0.7000	0.2006	0.2785	3.525	0.4131					
0.8000	0.2724	0.3654	2.957	0.3971					
0.9000	0.3970	0.5031	2.275	0.3699					
0.9300	0.4609	0.5680	2.023	0.3550					

$$\ln(\gamma_w w_1) = \ln \frac{p_1}{p_1^\circ} + \frac{B(p_1 - p_1^\circ)}{RT} \tag{2}$$

where B is the second virial coefficient of the solvent estimated by the Hayden–O'Connell method (*11*).

Flory–Huggins Parameters

The Flory–Huggins parameter χ (*5*) is defined by

$$\ln(\gamma_w w_1) = \ln \phi_1 + (1 - r_1/r_2) + \chi\phi_2^2 \tag{3}$$

where r_1 and r_2 are the chain lengths of the solvent molecule (1) and polymer molecule (2), respectively, estimated by

$$r_1/r_2 = M_1 v_1/M_2 v_2 \tag{4}$$

where M_1 and M_2 are the corresponding molar masses; the latter is the same as M_w.

Before calculating χ, VLE results for the two systems have been smoothed by a least-squares fit. Tables 4 and 5 list all the smoothed data, the corresponding ϕ_1 and γ_w and the calculated χ. It is shown from the tables that the Flory–Huggins parameter strongly depends on the concentration. For the system butyl acetate + polystyrene, χ increases as the concentration of the solvent increases. However, for the system diethyl ether + poly(butyl methacrylate), χ decreases as the concentration of the solvent increases. Besides, a notable molar-mass dependence for the Flory–Huggins parameter is observed. This is not a surprise for the system diethyl ether + poly(butyl methacrylate) because there is a remarkable molar-mass dependence for the VLE results. However, for the system butyl acetate + polystyrene, a weak molar-mass dependence still occurs.

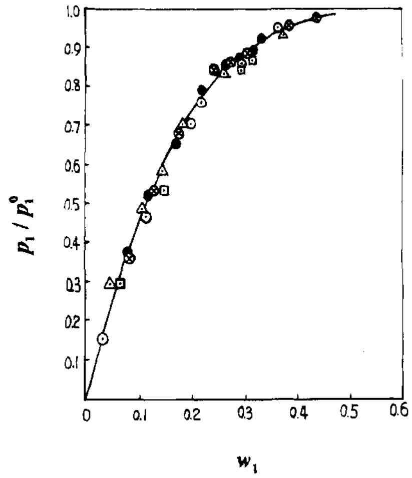

Figure 2. VLE for the system butyl acetate (1) + polystyrene (2): ⊙, $M_{w,2} = 3.84 \times 10^6$; ⊡, $M_{w,2} = 1.90 \times 10^5$; △, $M_{w,2} = 3.79 \times 10^4$; ⊗, $M_{w,2} = 9.10 \times 10^3$; ●, $M_{w,2} = 2.98 \times 10^3$.

Discussion and Conclusion

The Flory–Huggins parameters χ calculated from VLE results for the system butyl acetate + polystyrene given in Table 4 indicate that butyl acetate is not a good solvent for polystyrene. At infinite dilution, when w_1 approaches 1, χ will be far greater than 0.5. That means, the experimental temperature is much lower than the Θ temperature. On the other hand, χ shows a weak molar-mass dependence. When the molar mass is greater than

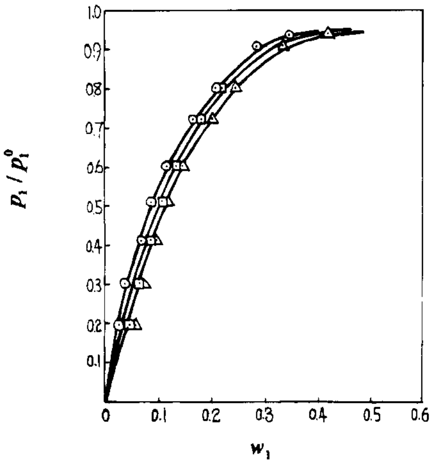

Figure 3. VLE for the system diethyl ether (1) + poly(butyl methacrylate) (2): ⊙, $M_{\rm w}3,_{2} = 88.1 \times 10^3$; ⊡, $M_{\rm w,2} = 37.9 \times 10^3$; △, $M_{\rm w,2} = 17.3 \times 10^3$.

about 10 000, the effect on χ can be virtually neglected. However, when the molar mass is small as shown by sample 5 ($M_{\rm w} = 2\ 980$), χ values are notably increased. The Flory–Huggins parameter χ measures the interaction between the solvent segment and the polymer segment. The lower the χ value, the stronger the interaction. Therefore, the longer chain length of the polymer in this system will enhance the solubility. However, the entropy effect caused by the chain length increasing is generally unfavorable to the solubility as shown by eqs 2 and 3. The pressure of the solvent p_1 will increase as the chain length of the polymer r_2 is increased. Therefore, the compensation between the interaction-energy effect and the entropy effect yields molar-mass-independent VLE results.

As for the system diethyl ether + poly(butyl methacrylate), the Flory–Huggins parameters χ calculated from VLE results shown in Table 5 indicate that diethyl ether is a good solvent for poly(butyl methacrylate). When w_1 approaches 1, χ will be less than 0.5. The experimental temperature is higher than the Θ temperature. On the other hand, χ shows a remarkable molar-mass dependence. The shorter chain length of the polymer, the smaller the χ value and the stronger the interaction between the solvent segment and the polymer segment will be. This indicates that the longer chain length is unfavorable to the solubility both from the interaction-energy effect and from the entropy effect. Remarkable molar-mass-dependent VLE results are then observed. The strong interaction between the ether group of the solvent and the ester group of the polymer perhaps is one of the reasons.

It can be concluded from this work that the dependence of the VLE results on the molar mass of the polymer is different for different systems. In practical application concerning VLE, the polydispersity of the polymer sample is not an important factor for the first system, butyl acetate + polystyrene, while for the second system, diethyl ether + poly(butyl methacrylate), the polydispersity of the polymer should be seriously considered.

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